INDIVIDUAL DETECTION OF GOLD NANOPARTICLES IN LIQUID USING PHOTOTHERMAL CORRELATION SPECTROSCOPY

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Gold nanoparticles are often employed as labels for biological systems or as functionalized units for biochemical sensors. Compared to other labels, such as fluorescent molecules and semiconductor nanocrystals, they have the advantage of not suffering from photobleaching or photoblinking. However, the photoluminescence quantum yield of gold nanoparticles is very low $(10^{-4} \text{ to } 10^{-5})$ and, thus, it is very difficult to apply single molecule fluorescence techniques for their detection. Photothermal detection provides an interesting alternative for the investigation of single non-luminescent nano-objects. In photothermal detection scheme, the sample is irradiated with a field resonant with the optical absorption spectrum of the nano-object. The photon energy absorbed is dissipated as heat into the environment generating a gradient of temperature around the particle that acts as a thermal lens. This effect is probed by another (non-resonant) field, which is scattered by the local changes in index of refraction.

By combining photothermal microscopy with a heterodyne detection scheme we achieve single-particle sensitivity for sizes down to a diameter of 20 nm. This size limit could be improved by using high numerical aperture optics, but for applications in high-throughput screening the enlarged detection volume used in the present work (approx. 200 fl) is preferable at the expense of better detection efficiency. We present illustrative results of Photothermal Correlation Spectroscopy for free gold nanoparticles in aqueous dispersions and in water-glycerol mixtures. The characteristic diffusion times retrieved from the correlation curves are in the order of tens of milliseconds for 80 nm particles in water and correspond to an average temperature increase of some tens of Kelvin. Increasing the power of the heating laser beam decreases the particle diffusion times, as expected. In back-scattering mode, the photothermal signal shows fast fluctuations arising from an interference effect between the backscattered and reference fields, which introduce a short component in the correlation function. This additional component is eliminated in forward-scattering mode and the signal to noise ratio also increases because the strength of the detected field is better suited to the detector employed. Changing to forward configuration allowed us to detect smaller-sized particles.

The results obtained with Photothermal Correlation Spectroscopy will be discussed in comparison with the more widely known technique of Fluorescence Correlation Spectroscopy (FCS), focusing on the difference between the physical nature of measured signals and its consequences for the respective correlation functions.

Figures:



Figure 1 – Graphical abstract.